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14. ABSTRACT The report summarizes the accomplishments by E. A. Carter during Dec. 1, 1999 to Nov. 30, 2002. New theories for describing the structure of electrons in condensed matter were developed: (i) a quantum mechanical embedding theory allows treatment of localized electronic excited states of adsorbates or impurities on and in metals; (ii) the most advanced kinetic energy density functional was derived, which allows for a linear scaling treatment of metallic electronic structure. Of more immediate interest to the Air Force are insights into the nature of metal-ceramic and ceramic-ceramic interfaces relevant to understanding the failure of thermal barrier coatings (TBC's). Alumina-nickel interfaces in the TBC's are predicted to be the weak links in these multicomponent/multilayered coatings. These fundamental insights led to proposed changes in the composition of the alloy bond coat lying between the metal engine component and the thermal insulating ceramic. In particular, promotion of open shell/covalent character at interfaces was suggested as a design principle to increase adhesion. To this end, early transition metals doped at the alumina-nickel alloy interface were predicted dramatically increase adhesion, and replacement of alumina by silica also starkly increased adhesion to both the nickel substrate and the zirconia top coat of the TBC.					
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**Final Technical Report for
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(Dec. 1, 1999 - Nov. 30, 2002)

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This grant supported the following research efforts:

- development of improved theories of condensed matter electronic structure
- applications of density functional theory (DFT) to metal-ceramic and ceramic-ceramic interfaces (in particular, zirconia, silica, and alumina with pure and doped nickel), with the goal of understanding how to design optimal protective coatings for jet engines.

We first summarize each contribution, and then present a publication list where more details of this work may be found, finally ending with a list of graduate students and postdoctorals involved in this work. The citation numbers here refer to the publication list that follows. Further details are available in earlier progress reports and in the published works cited below.

Advances in Condensed Matter Electronic Structure Theory

First Principles Embedding Theory

It is often sufficient to describe condensed matter electronic properties with the first-principles electronic structure technique in most common use today: density functional theory (DFT), in its various incarnations [7]. However, for certain classes of phenomena or materials, it is necessary to go beyond DFT to obtain even a qualitatively correct description (let alone, a quantitative one). To this end, we developed a means of embedding *ab initio* correlation methods – configuration interaction (CI), perturbation theory, or multiconfiguration self-consistent field (MCSCF) – into a periodically infinite DFT background. This allows a local region to be treated with the systematics and accuracy of quantum chemistry, while accounting for the infinite bulk material via DFT. The result is a way to systematically improve on ground state properties, such as adsorption or reaction energetics on a surface, beyond the results available from DFT. More intriguing is the prospect of treating local many-body excited states in condensed

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matter, a phenomenon that DFT cannot describe at all. Proof-of-principle calculations have been carried out for excited states of molecules on metal surfaces [4-6]. We have now begun to apply our embedding theory to gas-surface scattering phenomena that involve charge-transfer between the gas molecule and the metal surface (K. Niedfeldt, work in progress). We are collaborating with P. Nordlander at Rice University, where our calculations provide energies and lifetimes of excited states as the adsorbate approaches the metal surface; Nordlander then uses our results in a many-body theory of charge transfer to calculate ionization/neutralization probabilities. Other problems that involve local excited states or that require a many-body approach to electron correlation will also be examined, including: (i) the Kondo effect, which reduces the conductivity of metals due to a many-body excited state comprised of transition metal impurity electrons coupling to conduction electrons in nearly-free-electron-like metal hosts and (ii) strongly correlated oxides such as NiO (another system where DFT fails entirely - it predicts NiO to be a metal, whereas it is in fact a Mott-Hubbard insulator).

Linear Scaling Orbital-Free Density Functional Theory

We are interested in studying materials phenomena over length scales larger than the atom, including, for example: elucidating the true origin of hardening in ternary metal alloys, the mechanism of vacancy coalescence to form voids in shocked metals, etc. This cannot be done with conventional DFT, since its inherent cubic scaling with system size makes it prohibitively expensive to treat the number of atoms required to describe the phenomenon or the material.

Over the past half dozen years or so, we have been developing a linear scaling DFT method that can describe metallic states of matter. In particular, we focus on an "orbital-free" approach, which solves directly for the electron density, bypassing the calculation of orbitals [3]. Two quantities in conventional DFT usually are evaluated with orbitals present: the kinetic energy and the electron-ion energy, the latter when "nonlocal" pseudopotentials are employed. (The latter are used ubiquitously in solid-state DFT calculations in order to reduce the expense associated with representing the core electrons. They are potential operators that describe the valence electrons interaction with the core electrons + nucleus for each atom.) In an orbital-free approach, one must evaluate the kinetic energy as a functional only of the density and

one must use "local" pseudopotentials that only depend on position, r . If one could construct accurate kinetic energy density functionals (KEDF's) and accurate local pseudopotentials, then this orbital-free method could be applied to the entire periodic table, greatly simplifying calculations of electronic behavior (the orbital-free DFT method scales as $N \ln N$, where N is related to system size) for thousands of atoms.

In the late 1990's, we developed a new description of electron kinetic energy based on linear response theory, for use in orbital-free DFT (OF-DFT) calculations: our so-called linear-response-based KEDF with a density-dependent kernel [1]). This KEDF has only three parameters, two of which are determined universally from asymptotic analysis, leaving only one free parameter. This is to be contrasted with many functionals in the DFT world that end up as semi-empirical objects because they have so many empirically fitted parameters. In July 2002, there was an international CECAM workshop in Lyon on kinetic energy density functionals, where it was recognized that our functional was the state-of-the-art, the most accurate, and yet still practical, of all functionals yet proposed [2]. Its accuracy has been demonstrated for properties of surfaces and bulk crystals, even ones under shear, tensile, and compressive stress, at least for simple (non-transition) metals. We applied OF-DFT, e.g., to solve for the electron distribution of over a thousand atoms of a LiAl alloy, as well as metal nanocrystal arrays, where the number of atoms (~500) would have precluded a conventional DFT calculation. In the latter case, we predicted the onset of a metal-insulator transition in such an array, using a nonorthogonal tight binding model where the overlaps and energies were extracted from the orbital-free (OF) DFT calculation. The predicted particle spacing at which the transition occurs agreed well with experiment; moreover, we ascertained that this transition requires only very tiny overlaps of the particle wave functions, an observation not available from experiment [3].

Atomic Level Understanding of Thermal Barrier Coatings

We are interested in understanding how and why materials fail and then figuring out how to design materials that don't. To this end, we have been examining the interfaces between ceramics and metals, in order to suggest ways to improve the stability of ceramic coatings on metals. Such coatings are used to protect metal

components in harsh environments. This includes oxide ceramics on nickel alloys for use in thermal barrier coatings on jet engines [8, 11]. We are also examining impurities and dopants that segregate at interfaces, to understand which dopants may be useful and why, as well as how to treat the alloys in order to inhibit harmful chemical reactions that degrade the metals.

This work resulted in the filing of three provisional patents for improved coating (and catalyst) design. In them, we described ways to modify the metal alloy bond coating layer of a thermal barrier coating used to protect jet turbine engine components in order to enhance coating stability and extend its lifetime. After a patent search, it was determined that the two provisional patents related to improved coatings were very good ideas, but not new (General Electric had patents close enough that we could not proceed with filing the utility patent). However, the spin-off of the findings to catalyst design was original and the utility patent application was filed in 2003.

The most important findings of our materials interface work related to thermal barrier coatings were:

- The nature of bonding at the interface between metals and oxide ceramics was revealed for the first time. Prior to this work, it had been thought that electrostatics was responsible for the adhesion, with the prediction that more ionic oxides and/or thicker films would improve adhesion. However, our first principles calculations showed that the exact opposite is true: more covalent oxides form stronger bonds to metals and thicker films actually weaken adhesion, overthrowing the conventional wisdom [9, 10, 12-14]. In particular, it was found that alumina-nickel interfaces were the weakest, due to closed shell repulsions between the oxide ions in alumina interacting with the nearly-filled d-shell of nickel [13]. The more covalent zirconia formed stronger bonds to Ni, but they weakened with increasing film thickness [12]. The zirconia-alumina interface exhibited moderate adhesion, where the zirconia was prone to undergo a structural phase transition upon film thickening, which has been observed experimentally [9]. Upon heating to high temperatures, oxygen can be depleted from the alumina surface; we find that this surface exhibits metallic character [14], which should be taken into account for coatings that have undergone severe heat treatments.

- The above findings led to the hypothesis that doping metal – oxide ceramic interfaces with early transition metals [15-18] would enhance adhesion of the oxide coating to the metal. The idea was to promote open shell/covalent interactions across interfaces, which should enhance bonding. Our calculations confirmed that this was exactly correct. In particular, we examined the effect of doping zirconia/nickel and alumina/nickel interfaces with a half monolayer of Sc, Y, Ti, Al, and Zr between the two materials. The interfaces were allowed to completely relax; $\frac{1}{2}$ ML was the chosen dopant concentration because it is known that such dopants do segregate to these heterogeneous interfaces at such a level and it makes sense from a mechanical point of view (the early transition metals are larger than nickel and so submonolayer levels of dopant are required in order to not introduce compressive strain). We found that all the early transition metals improved the adhesion, while Al as a dopant weakened the interactions. We examined in great detail the bonding at the interface [17] and found that the open shell nature of the early transition metals allows donor-acceptor bonding between oxide ions and the dopant atoms to flourish. This increases the bonding beyond the polar covalent interactions between oxygen and localized metal and metal-metal interactions. Ni and Al do not have low-lying states that would permit such donor-acceptor interactions and hence the adhesion is less at interfaces with Ni and Al present [16, 18]. The effect is most pronounced for Ni/Al₂O₃ interfaces, which are very weak to begin with because of the very ionic (and hence closed shell) nature of alumina, but when doped these interfaces become up to twice as strongly adhered!
- We also proposed that using a more covalent oxide [19,20] in place of alumina may help adhesion of the thermal barrier coating. Due to its propensity to limit bulk oxygen diffusion similar to that of alumina, we considered silica as a possible replacement oxide. We find that the more covalent silica coating indeed is more strongly adhered to both interfaces that presently involve alumina: it is three times more strongly adhered to a nickel substrate and is twice as strongly adhered to the zirconia top coat. Thus, for some applications where water may

not be present in large quantities (which may destroy the silica), we suggest silica may be considered as an alternative oxidation barrier layer that may have longer lifetimes due to stronger adhesion.

Summary

During the last funding cycle, we made significant advances both in the area of new methods for describing condensed matter chemistry and physics [7] (our embedding theory extended to electronic excited states [4-6] and kinetic energy density functionals that afford a linear scaling treatment of metals [1-3]) and in uncovering the atomic level reasons for failure of thermal barrier coatings, as well as in putting forth suggestions for how to improve them. In particular, our thorough investigations have provided a deep understanding of the nature of metal-ceramic and ceramic-ceramic interfaces. We discovered, for example, that the weakest link in the thermal barrier coating is the interface between the thermally grown oxide scale (alumina) and the nickel-base superalloy substrate; this is quite consistent with electron microscopy that reveals voids forming at this interface after thermal cycling of the engine. These fundamental insights led us to propose changes in the alloy composition of the bond coat that lies between the metal engine component and the thermal insulating ceramic, involving either purposeful doping of the metal-ceramic interface with Ti or Zr or deposition of an alternative oxide (e.g., SiO_2) layer. These design principles may help increase the stability and hence the lifetime of TBC's in the future. Our current efforts are to explore several other dopants (Hf, Pt) and impurities (S) that are known players in the evolution of TBC's during use. Their roles are unclear at present; we hope to uncover the mechanisms of their actions in the next phase of this research.

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Participating Graduate Students and Postdoctoral Fellows

Graduate Students

Emily A. Asche Jarvis, Ph.D 2002. Dissertation title: *Atomic-level Culprits of Materials Failure: The Importance of Chemical Bonding at Heterogeneous Interfaces*. Available from UMI Proquest Digital Dissertaions <<http://wwwlib.umi.com/dissertations/gateway>>; all results contained in the thesis have been published in the open literature (see the list above). ACS Congressional Science Fellow 2002-03; Visiting Professor, Kenyon College, 2003-04.

Postdoctoral Fellows

Dr. Niranjana Govind. Now a Software Development Scientist at Accelrys, Inc.

Dr. Asbjorn Christensen. Now a Research Consultant at the Technical University of Denmark.

Dr. Stuart C. Watson. Now a Programmer/Systems Analyst in the Department of Chemistry and Biochemistry, UCLA.

Dr. Yan Alexander Wang. Now an Assistant Professor of Chemistry, University of British Columbia.

Dr. Frank Starrost. Now a Research Analyst at debis Systemhaus.

Dr. Thorsten Kluener. Now an Assistant Professor at the Fritz Haber Institute, Berlin.